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L3 L1 same (wafer or semiconductor or substrate) same (wet\$3 or  
liquid\$3 or solution or etch\$3)

21 L3

L2 L1 same turbulent\$3

8 L2

L1 gas same (intermit\$7 or ceas\$3) same bubbl\$3

1170 L1

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**PALM INTRANET****Inventor Name Search Result**

Your Search was:

Last Name = TSENG

First Name = WEN-HSIANG

Application#	Patent#	Status	Date Filed	Title	Inventor Name
<u>10286626</u>	Not Issued	030	11/02/2002	APPLICATION OF IMPRESSED-CURRENT CATHODIC PROTECTION TO PREVENT METAL CORROSION AND OXIDATION	TSENG, WEN-HSIANG
<u>10143053</u>	Not Issued	030	05/09/2002	FERRIS WHEEL-LIKE STRIPPING OR CLEANING MECHANISM FOR SEMICONDUCTOR FABRICATION	TSENG, WEN-HSIANG
<u>10140740</u>	Not Issued	030	05/07/2002	METHOD AND APPARATUS FOR THICK FILM PHOTORESIST STRIPPING	TSENG, WEN-HSIANG
<u>10127086</u>	Not Issued	030	04/22/2002	FLUSH SYSTEM FOR DRY FILM PHOTORESIST REMOVER	TSENG, WEN-HSIANG
<u>09996335</u>	Not Issued	030	11/21/2001	FILLER FOR AIRTIGHT CONTAINER	TSENG, WEN-HSIANG
<u>09629213</u>	Not Issued	071	07/31/2000	PHOTORESIST STRIPPER USING NITROGEN BUBBLER	TSENG, WEN-HSIANG
<u>08767117</u>	<u>5820689</u>	150	12/04/1996	WET CHEMICAL TREATMENT SYSTEM AND METHOD FOR CLEANING SUCH SYSTEM	TSENG, WEN-HSIANG

Inventor Search Completed: No Records to Display.

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Wen-Hsiang

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**PALM INTRANET****Inventor Name Search Result**

Your Search was:

Last Name = CHEN

First Name = CHIE-CHI

Application#	Patent#	Status	Date Filed	Title	Inventor Name
<u>09629213</u>	Not Issued	071	07/31/2000	PHOTORESIST STRIPPER USING NITROGEN BUBBLER	CHEN, CHIE-CHI
<u>09591846</u>	<u>6281140</u>	150	06/12/2000	METHOD OF REDUCING THE ROUGHNESS OF A GATE INSULATOR LAYER AFTER EXPOSURE OF THE GATE INSULATOR LAYER TO A THRESHOLD VOLTAGE IMPLANTATION PROCEDURE	CHEN, CHIE-CHI
<u>09325307</u>	<u>6360756</u>	150	06/03/1999	WAFER RINSE TANK FOR METAL ETCHING AND METHOD FOR USING	CHEN, CHIE-CHI

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**PALM INTRANET**

## Inventor Name Search Result

Your Search was:

Last Name = PAN

First Name = SHENG-LIANG

Application#	Patent#	Status	Date Filed	Title	Inventor Name
<u>10209149</u>	Not Issued	030	07/30/2002	NOVEL MATERIAL TO IMPROVE CMOS IMAGE SENSOR YIELD DURING WAFER SAWING	PAN, SHENG-LIANG
<u>10140740</u>	Not Issued	030	05/07/2002	METHOD AND APPARATUS FOR THICK FILM PHOTORESIST STRIPPING	PAN, SHENG-LIANG
<u>10124998</u>	Not Issued	030	04/18/2002	NOVEL BUMP REFLOW METHOD BY INERT GAS PLASMA	PAN, SHENG-LIANG
<u>10032341</u>	Not Issued	093	12/21/2001	METHOD OF MAKING A BUMP ON A SUBSTRATE USING MULTIPLE PHOTORESIST LAYERS	PAN, SHENG-LIANG
<u>09961557</u>	Not Issued	030	09/24/2001	NOVEL METHOD TO ENHANCE THE ADHESION BETWEEN DRY FILM AND SEED METAL	PAN, SHENG-LIANG
<u>09902894</u>	Not Issued	094	07/12/2001	METHOD FOR FORMING MICRO LENS STRUCTURES	PAN, SHENG-LIANG
<u>09867094</u>	Not Issued	161	05/30/2001	METHOD TO FORM THE RING SHAPE CONTACT TO CATHODE ON WAFER EDGE FOR ELECTROPLATING IN THE BUMP PROCESS WHEN USING THE NEGATIVE TYPE DRY FILM PHOTORESIST	PAN, SHENG-LIANG
<u>09835027</u>	<u>6468704</u>	150	04/16/2001	METHOD FOR IMPROVED PHOTOMASK ALIGNMENT AFTER EPITAXIAL PROCESS THROUGH 90	PAN, SHENG-LIANG

				DEGREE ORIENTATION CHANGE	
<u>09726740</u>	Not Issued	121	11/30/2000	SELECTIVE ELECTROPLATING METHOD EMPLOYING ANNULAR EDGE RING CATHODE ELECTRODE CONTACT	PAN, SHENG-LIANG
<u>09693505</u>	<u>6274917</u>	150	10/23/2000	HIGH EFFICIENCY COLOR FILTER PROCESS FOR SEMICONDUCTOR ARRAY IMAGING DEVICES	PAN, SHENG-LIANG
<u>09679514</u>	Not Issued	061	10/06/2000	METHOD TO IMPROVE PASSIVATION OPENINGS BY REFLOW OF PHOTORESIST TO ELIMINATE TAPE RESIDUE	PAN, SHENG-LIANG
<u>09664421</u>	Not Issued	030	09/18/2000	METHOD TO MONITOR STEPPER LENS QUALITY IN COLOR FILTER PROCESS	PANG, SHENG-LIANG
<u>09633644</u>	Not Issued	083	08/07/2000	HIGH TRANSMITTANCE OVERCOAT FOR OPTIMIZATION OF LONG FOCAL LENGTH MICROLENS ARRAYS IN SEMICONDUCTOR COLOR IMAGERS	PAN, SHENG-LIANG
<u>09629213</u>	Not Issued	071	07/31/2000	PHOTORESIST STRIPPER USING NITROGEN BUBBLER	PAN, SHENG-LIANG
<u>09593537</u>	<u>6395576</u>	150	06/14/2000	HIGH EFFICIENCY COLOR FILTER PROCESS TO IMPROVE COLOR BALANCE IN SEMICONDUCTOR ARRAY IMAGING DEVICES	PAN, SHENG-LIANG
<u>09591846</u>	<u>6281140</u>	150	06/12/2000	METHOD OF REDUCING THE ROUGHNESS OF A GATE INSULATOR LAYER AFTER EXPOSURE OF THE GATE INSULATOR LAYER TO A THRESHOLD VOLTAGE IMPLANTATION PROCEDURE	PAN, SHENG-LIANG
<u>09547546</u>	<u>6417022</u>	150	04/12/2000	METHOD FOR MAKING LONG FOCAL LENGTH	PAN, SHENG-LIANG

				MICRO-LENS FOR COLOR FILTERS	
<u>09414926</u>	<u>6495813</u>	150	10/12/1999	MULTI-MICROLENS DESIGN FOR SEMICONDUCTOR IMAGING DEVICES TO INCREASE LIGHT COLLECTION EFFICIENCY IN THE COLOR FILTER PROCESS	PAN , SHENG-LIANG
<u>09414925</u>	<u>6171885</u>	150	10/12/1999	HIGH EFFICIENCY COLOR FILTER PROCESS FOR SEMICONDUCTOR ARRAY IMAGING DEVICES	PAN , SHENG-LIANG
<u>09408701</u>	Not Issued	161	09/30/1999	METHOD FOR FORMING MICRO LENS STRUCTURES	PAN , SHENG-LIANG
<u>09325307</u>	<u>6360756</u>	150	06/03/1999	WAFER RINSE TANK FOR METAL ETCHING AND METHOD FOR USING	PAN , SHENG-LIANG
<u>09298936</u>	<u>6143579</u>	150	04/26/1999	EFFICIENT METHOD FOR MONITORING GATE OXIDE DAMAGE RELATED TO PLASMA ETCH CHAMBER PROCESSING HISTORY	PAN , SHENG-LIANG
<u>09221958</u>	Not Issued	071	12/28/1998	PLASMA ETCH METHOD FOR FORMING UNIFORM LINEWIDTH RESIDUE FREE PATTERNED COMPOSITE SILICON CONTAINING DIELECTRIC LAYER/SILICON STACK LAYER	PAN , SHENG-LIANG
<u>09152349</u>	<u>6107202</u>	150	09/14/1998	PASSIVATION PHOTORESIST STRIPPING METHOD TO ELIMINATE PHOTORESIST EXTRUSION AFTER ALLOY	PAN , SHENG-LIANG
<u>08977190</u>	<u>6103633</u>	150	11/24/1997	METHOD FOR CLEANING METAL PRECIPITATES IN SEMICONDUCTOR PROCESSES	PAN , SHENG-LIANG
<u>08843947</u>	<u>5880019</u>	150	04/17/1997	INSITU CONTACT DESCUM FOR SELF-ALIGNED CONTACT PROCESS	PAN , SHENG-LIANG
<u>08682481</u>	<u>5776832</u>	150	07/17/1996	ANTI-CORROSION ETCH PROCESS FOR ETCHING METAL	PAN , SHENG-LIANG

				INTERCONNECTIONS EXTENDING OVER AND WITHIN CONTACT OPENINGS	
<u>08496017</u>	<u>5556806</u>	150	06/28/1995	SPIN-ON-GLASS NONETCHBACK PLANARIZATION PROCESS USING OXYGEN PLASMA TREATMENT	PAN , SHENG-LIANG

**Inventor Search Completed: No Records to Display.**

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**PALM INTRANET****Inventor Name Search Result**

Your Search was:

Last Name = FANG

First Name = JEN-SHIANG

Application#	Patent#	Status	Date Filed	Title	Inventor Name
09629213	Not Issued	071	07/31/2000	PHOTORESIST STRIPPER USING NITROGEN BUBBLER	FANG, JEN-SHIANG

**Inventor Search Completed: No Records to Display.**

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DETAILED DESCRIPTION

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## [Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the medical fluid art using the processing medical fluid which performs etching or washing of a semiconductor substrate, and the medical fluid concerned in manufacture processes, such as a semiconductor device.

[0002]

[Description of the Prior Art] In manufacture processes, such as a semiconductor device, the medical fluid which raised the ratio of a hydrogen peroxide rather than the medical fluid which mixed aqueous ammonia, 30-% of the weight hydrogen peroxide solution, and ultrapure water to 1:1:5 by the volume ratio 30% of the weight, or this ratio is usually used for the purpose of the particle of a semiconductor substrate front face, and removal of the organic substance. The mixed conditions of the aforementioned medical fluid are decided as a result of trial and error in balance with washing nature and the granularity of the semiconductor substrate front face after washing. Washing of the semiconductor substrate by the medical fluid concerned is performed by heating the medical fluid concerned to about 60 degrees C, and each medical fluid concentration in a washing tub changes with time towards decreasing by those evaporation, decomposition, etc. Therefore, the stability of washing is secured by processing a wafer, performing a medical fluid supplement for every fixed time. In JP,7-142435,A, the way change of the etch rate to ammonia concentration washes in the concentration field to 2.0 to few 3.5 % of the weight is indicated.

[0003] In JP,63-274149,A, what contains the fourth class ammonium hydroxide as a processing agent used for washing processing of a semiconductor etc. is indicated. Moreover, instead of the hydrogen peroxide, the art using ozone is indicated by JP,1-99221,A etc. as an oxidizer.

[0004]

[Problem(s) to be Solved by the Invention] Although the medical fluid in a processing tub will be total-exchanged by the washing method which uses the penetrant remover which carried out hydrogen-peroxide content with ammonia if it results in the stage which a throughput does not recover even if it performs the stage or the supplement to which contamination of the medical fluid in a processing tub usually progressed, compared with the amount of medical fluids supplied to a processing tub at the time of the total exchange, it is by no means few in the supplement total amount of the medical fluid supplied by the total exchange. By the method of JP,7-142435,A, a supplement is not performed until ammonia concentration becomes 2.0 or less % of the weight, but the supplement interval is extended till 100 minutes. however, the method concerned is supplying so that it may become 3.5% of the weight, when 100 parts are passed, although the effect was on the stable disposition of medical fluid processing, and the effect of curtailment of the amount of supplements is small As long as ammonia with high vapor pressure is used as alkali, it is hard to avoid the concentration fall by volatilization, and it must add water at the same time it fills up a medical fluid as alkali or an oxidizer, since each commercial medical fluid is about 30 % of the weight, and ammonia and a hydrogen peroxide must supply in consideration of dilution by supplement.

[0005] The fourth class ammonium hydroxide which the processing agent of JP,63-274149,A contains has vapor pressure lower than ammonia, and the concentration fall of the alkali component by volatilization can be improved sharply. However, a hydrogen peroxide is indispensable, in order for the processing agent concerned to contain the hydrogen peroxide and surfactant other than the fourth class ammonium hydroxide and to suppress an etch rate. Since, as for a hydrogen peroxide, concentration decreases with time progress according to an autolysis in the chemical reaction row of wafer processing, a hydrogen peroxide needs to be supplied also in this case.

[0006] Ozone can be easily prepared by using a commercial ozone generator in the manufacture site of a semiconductor device. Therefore, if ozone is used as a peroxidation agent instead of a hydrogen peroxide, curtailment of the manufacturing cost by medical fluid purchase can be aimed at. In addition, it excels also in the point that dilution by medical fluid supplement does not occur like a hydrogen peroxide. However, the concentration fall by volatilization is not avoided, but in order to be stable medical fluid processing, the supplement of ammonia is indispensable, as it already said that ammonia is used as alkali like the method currently indicated by JP,1-99221,A etc. Moreover, it is mentioned in JP,8-12488,A that ammonia oxidizes by ozone and carries out concentration reduction with time progress as a trouble of this method.

[0007] In JP,8-12488,A, the method of using for alkali the tetramethylammonium hydroxide which does not oxidize by ozone is indicated, and if a hydrogen peroxide is used together as an oxidizer according to the official report concerned, it is supposed that ozone efficiency can be gathered. However, according to examination by the artificer, in the case of Si substrate, an etch rate is quick, the granularity on the front face of a substrate after processing was large, and it became clear that it is not suitable for manufacture of the semiconductor device of the super-high accumulation demanded to stop the surface roughness after processing by the method which does not contain a hydrogen peroxide among JP,8-12488,A. Although the problem of surface roughness will improve if a hydrogen peroxide is used together, the problem by using an above-mentioned hydrogen peroxide arises.

[0008] this invention has little change with time in a throughput, and aims at offering the medical fluid art using the processing medical fluid which can perform etching of a semiconductor substrate, or washing lotion liquid processing, and the medical fluid concerned by the few medical fluid supplement for a long time.

[0009]

[Means for Solving the Problem] The artificer performed various examination about washing processing of Si semiconductor substrate by the mixed medical fluid of an alkaline medical fluid and an oxidizing quality medical fluid, and discovered the following facts.

[0010] Being able to express the washing capacity of a medical fluid by the etch rate on the front face of a substrate (it considers as  $dR/dt$  below),  $dR/dt$  is OH in a medical fluid. - It is set by the function depending on concentration and processing temperature. In etching of Si substrate or a metal membrane, there are oxidization, a reaction (the 1st reaction) to which the dissolution progresses gradually, and a reaction (the 2nd reaction) to which oxidization and the dissolution progress simultaneously. Oxidizer concentration is OH. - In being larger than concentration, the 1st reaction progresses to dominance. Oxidizer concentration is [ a low and ] OH. - The 2nd reaction which participates in both oxidization and the dissolution progresses. In the case of Si substrate, etching at the 2nd reaction is anisotropic etching, and progresses quickly far rather than what is depended on the 1st reaction. Therefore, if washing processing of Si substrate is performed on conditions to which contribution of the 2nd reaction becomes large, surface roughness will increase. It is desirable to perform washing processing on conditions which do not almost have contribution of the 2nd reaction, and, for that, it is OH. - After holding down concentration to 10 to 3 or less mol/l, it is required for an oxidizer with existence of the oxidizer which can oxidize Si substrate front face, i.e., strong oxidizing power, to be sufficient concentration at the speed exceeding the 2nd reaction. However, in order to secure washing nature, it is not concerned with the concentration of an oxidizer, but it is OH. - It is required for concentration to be 10 to 5 or more mol/l.

[0011] this invention is made by the rule found out by the aforementioned artificer and the hydroxide

row of the fourth class ammonium based on the matter property of ozone. the processing medical fluid of the semiconductor substrate of this invention The fourth class ammonium hydroxide and ozone are contained, and it is OH. - Concentration is  $10^{-5}$  -  $10^{-3}$  mol/l. It is characterized by an ozone level being 10 to 5 or more mol/l, and it is desirable for the fourth class ammonium hydroxide concentration to be  $10^{-3}$  - 1 mol/l. As the fourth class ammonium hydroxide, a tetramethylammonium hydroxide is suitable. further Weak-acid ion content is carried out and the weak-acid ion concerned is Above OH. - While performing autolysis, volatilization, the thing that does not cause the fall of concentration by the reaction with ozone, or processing in concentration conditions, it is desirable for the concentration fall concerned to be slight.

[0012] Moreover, in the medical fluid art of a semiconductor substrate, the fourth class ammonium hydroxide solution of the specified quantity is supplied to a medical fluid processing tub, next it is OH. - So that concentration may turn into predetermined concentration between  $10^{-5}$  -  $10^{-3}$  mol/l Supply an organic acid or an inorganic acid, next, adjust an oil level by ultrapure water, and, more nearly next than an ozonator, bubbling of the ozone content gas is carried out to the medical fluid concerned. After carrying out the temperature up of the medical fluid concerned to the predetermined temperature of 90 degrees C or less and reaching predetermined temperature, the ozone content gas concerned next, continuation or by carrying out the predetermined-time dipping of the semiconductor substrate of a processing object to the processing medical fluid concerned, supplying intermittently As for formic acid, an acetic acid, a propionic acid, and an inorganic acid, it is [ the aforementioned organic acid which performs etching or washing processing of a semiconductor substrate ] desirable to use a hydrofluoric acid, a hydrochloric acid, a nitric acid, a sulfuric acid, a phosphoric acid, and a boric acid. Or the fourth class ammonium hydroxylation solution of the specified quantity is supplied to a medical fluid processing tub, and, next, it is OH. - So that concentration may turn into predetermined concentration between  $10^{-5}$  -  $10^{-3}$  mol/l Blow a sour gas or a carbon dioxide and, next, an oil level is adjusted by ultrapure water. From an ozonator, carry out bubbling of the ozone content gas to the medical fluid concerned, and, next, the temperature up of the medical fluid concerned is carried out to the predetermined temperature of 90 degrees C or less. After reaching predetermined temperature, the ozone content gas concerned the semiconductor substrate of a processing object to the processing medical fluid concerned continuation or by carrying out the dipping of the predetermined-time semiconductor substrate, supplying intermittently It is characterized by performing etching or washing processing of a semiconductor substrate, and the aforementioned sour gas is a hydrogen chloride, hydrogen fluoride, NOX, and SOx. Using is desirable.

[0013] It is desirable to use for a medical fluid supplement the ultrapure water which made the further carry out the saturation dissolution of the ozone beforehand at the medical fluid manufacture row within a processing tub.

[0014]

[Embodiments of the Invention] Next, the gestalt of operation of this invention is explained with reference to a drawing.

[0015]

[Example]

Example 1 drawing 1 shows the particle removal performance at the time of processing Si semiconductor substrate with the medical fluid of this invention, and the surface roughness on the front face of a substrate after processing. Processing temperature is 65 degrees C and the processing time is for 10 minutes. A solid line is based on the manufacture conditions of this invention, and a dashed line portion is OH from the manufacture conditions of this invention. - The case where it prepares so that concentration may become low or high is shown. It is concentration set to the processing medical fluid of the semiconductor substrate of this invention, and predetermined [ between  $10^{-3}$  - 1 mol/l ] in the concentration of the hydroxide of the fourth class ammonium, and is OH in a processing medical fluid. - So that concentration may become  $5 \times 10^{-5}$  -  $1 \times 10^{-3}$  mol/l The OH concerned - Although autolysis, volatilization, and the medicine for neutralization (what works as an acid to ammonia) to which a concentration fall contains the slight matter by the reaction with ozone are added on concentration

conditions and an ozone level is performed by 10 to 5 or more mol/l Using a tetramethylammonium hydroxide as the fourth class ammonium hydroxide, the concentration performs by ten to 2 mol/l., and an ozone level performs the result of drawing 1 by  $5 \times 10^{-4}$  to  $4 \times 10^{-4}$  mol/l. By making a medical fluid carry out the saturation dissolution of the ozone especially at the time of manufacture, during processing, ozone is supplied from the bottom of the tank section so that the saturation dissolution can be maintained, and it is OH. - When the medical fluid concerned was prepared so that concentration may become  $2.5 \times 10^{-4}$  mol/l, the particle removal performance equivalent to conventional ammonia and the mixed medical fluid of a hydrogen peroxide was obtained, and surface roughness was also of the same grade.

[0016] Although the fourth class ammonium hydroxide is not limited to a tetramethylammonium hydroxide, the carbon number of an alkyl group can use three or less thing desirably [ a thing long-chain in an alkyl group ] in respect of solubility. The tetramethylammonium hydroxide which a high grade thing tends to receive was the most desirable to semiconductor manufacture, and used the tetramethylammonium hydroxide for the drawing 1 row also in the experiment of below-mentioned drawing 2 at it.

[0017] Of course, the common acid as the aforementioned medicine for neutralization can also use a sour gas and a carbon dioxide. For example, it was able to skin as an acid and carboxylic acids, such as an acid, an acetic acid, and a propionic acid, a hydrofluoric acid, a hydrochloric acid, the nitric acid, the sulfuric acid, the phosphoric acid, and the boric acid were able to be used. A medical fluid is OH when a phosphoric acid is used for weak-acid rows, such as the aforementioned carboxylic acid, and a hydrofluoric acid, a boric acid. - It has buffer capacity about concentration and is OH under processing. - The stability of concentration was high. Moreover, a carbon dioxide is blown and it is OH. - A medical fluid is OH when concentration is prepared. - It has buffer capacity about concentration and is OH under processing. - The stability of concentration was high.

[0018] What blew the ozone content gas beforehand generated from the ozonator within the depot into the ultrapure water used for dilution, and carried out the saturation dissolution of the ozone was used. Bubbling of the ozone content gas generated from the ozonator was carried out from the processing bottom of the tank section during processing of Si semiconductor substrate.

[0019] Example 2 drawing 2 shows concentration change of the alkali component at the time of carrying out consecutive processing of the semiconductor substrate, without supplying. By this experiment, tetramethylammonium-hydroxide concentration is 10-2 mol/l and OH. - It prepared so that concentration might become  $2.5 \times 10^{-4}$  mol/l and an ozone level might become  $5 \times 10^{-4}$  mol/l. In addition, only addition of ultrapure water was performed for oil-level maintenance. In the case of conventional ammonia and the mixed medical fluid of a hydrogen peroxide, the ammonia which cannot perform medical fluid processing stabilized without the supplement, but is emitted during processing at a jet pipe is great. On the other hand, in the processing medical fluid of this invention, 90% or more remained at the time after the 2-hour progress from which remains of ammonia become 10% or less with conventional ammonia and the mixed medical fluid of a hydrogen peroxide.

[0020] In washing aiming at the particle removal by the medical fluid concerned, loss by volatilization and the autolysis of the medical fluid component under processing is conspicuous compared with the conventional technology, it is small, and the life of a medical fluid is long and there are also very few supplements of the medical fluid under processing. On the other hand, the particle removal performance is equivalent to the conventional technology, and the increase in the granularity on the front face of a substrate after processing is also of the same grade as the conventional technology. Since composition change is small, the medical fluid throughput is also stable, and the yield of a semiconductor device and reliability can be improved. Furthermore the amount of the medical fluid used can be cut down sharply, and the cost of medical fluid purchase and the processing cost of a waste medical fluid can be reduced sharply. As for this, maintenance of the earth environment which poses a problem simultaneously these days is also effective.

[0021]

[Effect of the Invention] As explained above, according to this invention, a medical fluid throughput is stabilized and the yield of a semiconductor device and improvement in reliability can be performed. In

addition, when the amount of the medical fluid used can be suppressed and the cost of medical fluid purchase and the processing cost of a waste medical fluid can be cut down, an environmental load can contribute to maintenance of earth environment small.

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[Translation done.]